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R434-2010


**Imperial Oil/CPPI Bio-diesel Research Project
Funded Under NRDDI Program**

16th Annual MDEC Conference

October 5, 2010

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Imperial Oil/CPPI Renewable Diesel Fuel Program

Research program scoped to address concerns with FAME bio-diesel

- Low temperature operability (HD on-road application)
- Fuel storage at low temperature (all applications)
- Thermal/oxidation/storage stability of bio furnace fuel
- Canola, Soybean, Tallow and Palm Methyl Esters included in study

Program builds upon existing expertise & leveraged by on-going work within and outside the company

- Performance in light duty engines (Europe)
- Optimum additives for cold flow, oxidation control...etc (Additive Suppliers)
- Low temperature operability of SME and TME in on-road HD engines (CRC 650)
- Low temperature operability in on-road HD engines (IOL/CPPI SAE 2008-01-2380)
- Long term operability of B2 & B5 diesel in on-road HD engines (ARDD)
- Test method appropriateness/method development (ASTM, NREL, CEN...etc)

Presentation will report on the work to date with focus on

- Phase separation above the cloud point

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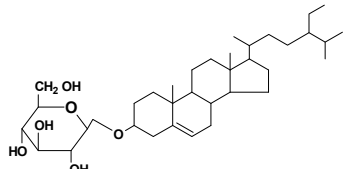
Phase Separation Above the Cloud Point – Saturated Monoglycerides

- ❑ **Flint Hills Resources (IASH 2007, Tuscon, AZ)**
 - Plugging of Dispensing filters (nominal 30µm) at -18°C with B2.5 using BQ9000 compliant B100 SME
 - Filter plugging caused by saturated monoglycerides (SMG)
- ❑ **Infineum (April 2008 Presentation by Davis & Denecker)**
 - Precipitation above CP seen with all FAME in Bx – FBT (IP 387) used to detect
 - Filter plugging attributed to SMG in add-back experiments
- ❑ **Cosmo Oil Co. Ltd (SAE 2008-01-2505)**
 - Low temperature storage testing in lab & AWCD with B5 PME(3), B5 SME , B5 RME
 - B5 PME stored at 10°C produced crystals of C14 to C18 monoglycerides
 - Authors concluded that SMG was the cause and its content in FAME needs to be limited
- ❑ **B5 SME Filter Blocking Problem at US Terminal**
 - Occurred in above-ground tanks at 0-15°F with 10 µm mesh filter dispensing pumps
 - Cause attributed to SMG

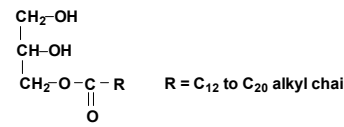
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Problematic Impurities Found in Bio-Diesel (FAME)




Sterol Glucoside m.p. = 240°C



monoglycerides R = C₁₂ to C₂₀ alkyl chain

- ❑ Sterol glucosides occur naturally in vegetable oils
 - Present at 10 to 120 wppm in crude FAME
 - Limit controlled by the Cold Soak Filtration Test (ASTM D7501)
- ❑ Monoglycerides are the result of incomplete trans-esterification
 - Current limits for monoglycerides in FAME:
 - No limit in ASTM D 6751
 - 0.8 wt% max EN 14214
 - 0.5 wt% max balloted at CGSB
 - Saturated monoglycerides have been implicated in filter plugging (m.p. = 71 - 81°C)
 - Currently no spec limit on saturated monoglycerides


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Cold Soak Filtration Test and Filter Blocking Tendency Test

- Cold Soak Filtration Test (ASTM D7501)**
 - Apply to B100 (FAME)
 - FAME soaked at 4.4°C (40°F) for 16 hours
 - 3 or more hours to warm up to 20-22°C
 - Filter 300 mL, 47 mm diameter, 0.7µm glass fiber filter, 78kPa
 - ASTM D 6751 Pass if CSFT is < 360 sec and < 200 sec for operability < -12°C
 - CGSB ballot is csft < 200 sec.
- Filter Blocking Tendency Test (ASTM D2068)**
 - Apply to B0 – B100
 - Filter 300 mL at a rate of 20 mL/min
 - 13 mm diameter, 1.6µm glass fiber filter
 - "Pass" considered to be FBT ≤ 1.4
 - 300 mL has been filtered and pressure is ≤ 105 kPa

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Low Temperature Storage Stability - Lab Program

Objective

To address wax settling and precipitation of material above the cloud point which could have significant impact on field performance

Test Protocol

Set # 1: Storage at 2-4°C above blend cloud point but below FAME cloud pt for 10 days


Set # 2: Storage at 1°C for 10 days

- Appearance (1 day, 2 day, 4 day, 5 day and 10 day)
- Warm up then Filter Blocking Tendency (ASTM D2068)

Fuels & FAME's

- Six Canadian low cloud ULSD fuels (LSD-25 to LSD-48)
- Aromatics content from 0 to 43 wt%
- CME, SME, TME and PME at B0, B2, B5 and B20
- Total of 57 fuels
- Properties of base fuels and FAME available upon request

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Correlation Between SMG Content and Filter Blocking Tendency

- FBT increases with increasing SMG content in the fuel
- Relatively good correlation between FBT and SMG (R2 = 0.85)
 - The CSFT of the PME used was >720 secs

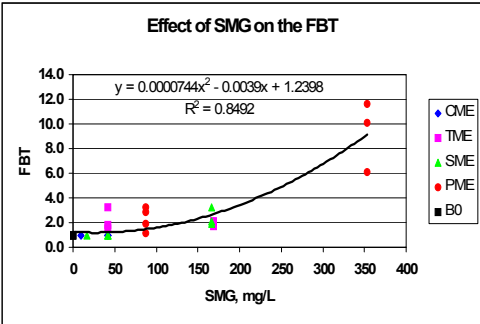
$$SMG_{mg/L} = FAME_{vol\%} \times d_{FAME} \times SMG_{mg/kg}$$

SMG_{mg/L} = SMG in the fuel


FAME_{vol%} = Volume of FAME in the fuel

d_{FAME} = FAME density

SMG_{mg/kg} = SMG in the FAME



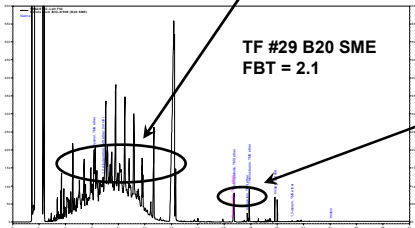
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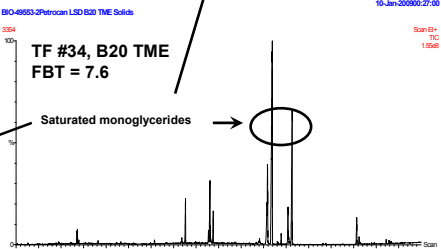
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GC-MS Confirms SMG as Cause of High FBT

- GC-MS analysis confirmed the enrichment of SMG in the filter residue
 - 1-monopalmitin
 - 2- monopalmitin
 - 1-monostearin
 - 2-monostearin
- Presence of residual fuel

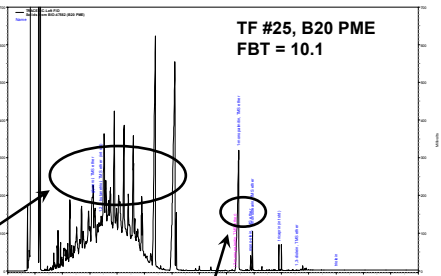


TF #29 B20 SME
FBT = 2.1



TF #34, B20 TME
FBT = 7.6

Saturated monoglycerides



TF #25, B20 PME
FBT = 10.1

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Effect of SMG on the Operability of Class 8 Trucks Tested in AWCD

- 3 Class 8 trucks equipped with most popular engines**

Vehicle	Truck	Engine	Year
Freightliner	D	Detroit Diesel Series 60	2004
International	A	Cummins ISM	2005
International	B	Cummins ISM	2005


- Fuel delivery system found critical for low temperature operability**
 - DD Series 60 has one 7 µm filter and 220W electric heater in fuel filter housing under the hood
 - Cummins ISM has one 7 µm filter outside cabin and no electric heater. Lower fuel recirculation than DD Series 60
- Test fuel: B5 CME spiked with 150, 200 and 250 mg/L SMG (Total 18 tests)**
 - SMG was added to the CME and heated to 70 -80°C for 3-4 hours prior to blending into base fuel @ 5%
 - Base fuel is commercially available in Ontario
 - Pre-soaked at -16°C for 84-90 hours prior to the test
- Test condition: -16°C (10°C above -26°C cloud point of fuel)**
 - 10 minutes idle followed by 1 hour at 80 kph steady speed
- Decision on the next test based on the ΔP across the filter**
 - Repeat or continue next test with "old" filter
- Failure = rough start, stall at idle and failure to reach 80 kph**

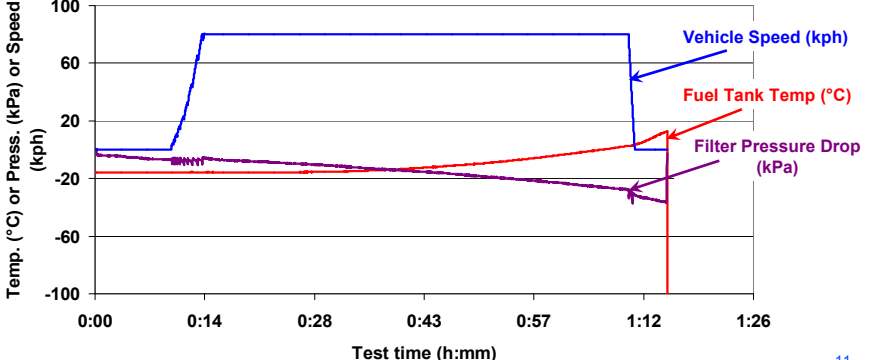
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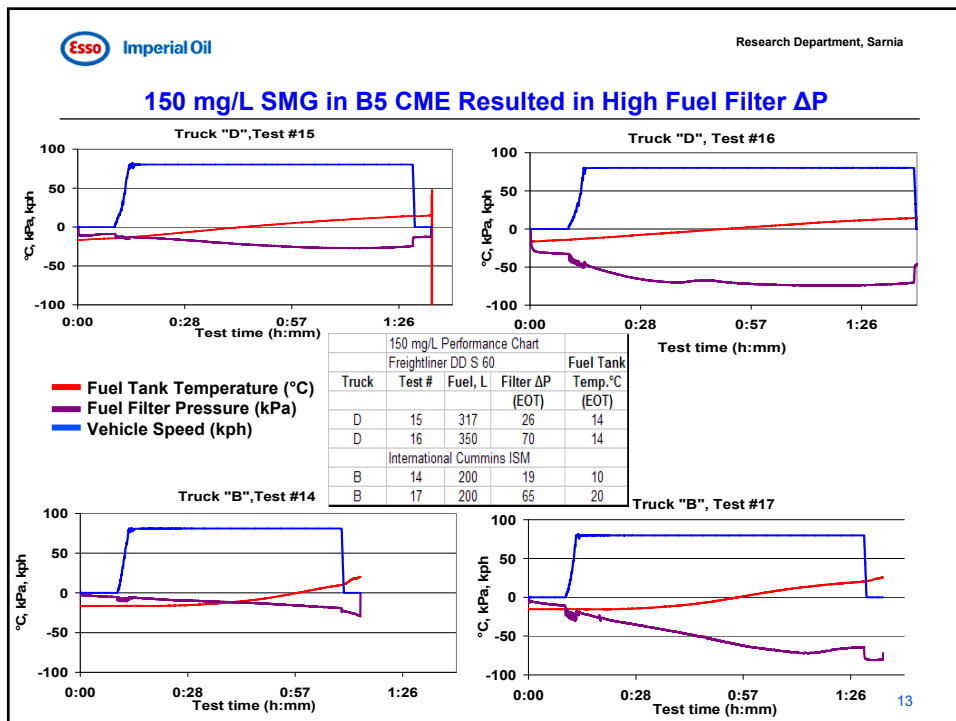
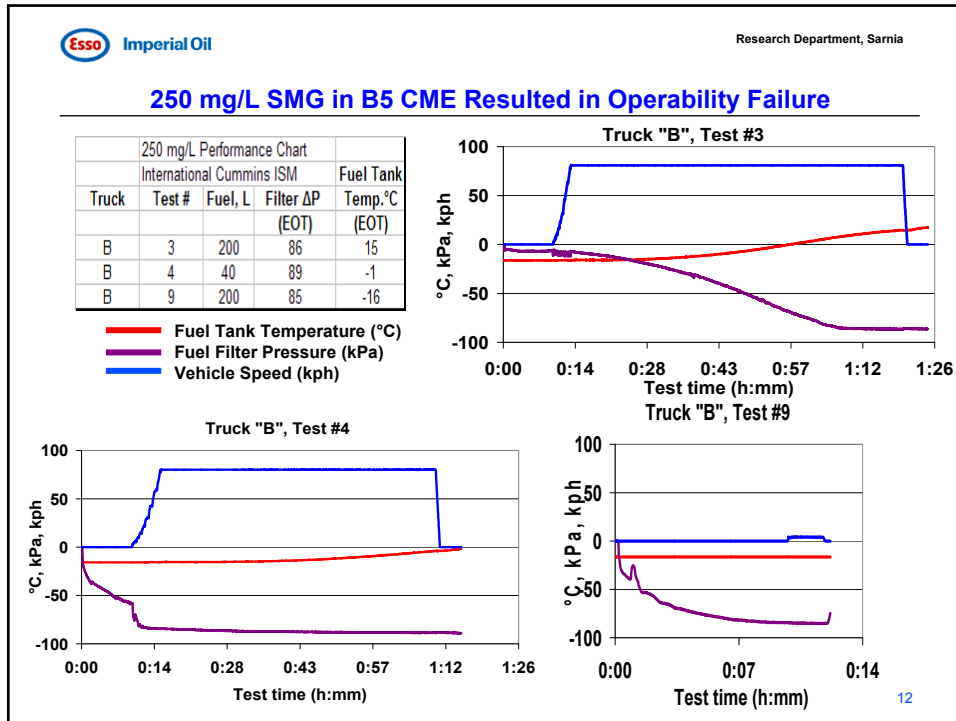
Key Parameters Measured in AWCD Test

- Test cell and pre-soak chamber can be controlled independently from - 40 °C to +43 °C
- Specified computer controlled cool-down profile or fast cool-down rate
- Wind velocity can be synchronized to vehicle speed or independently controlled to 120kph





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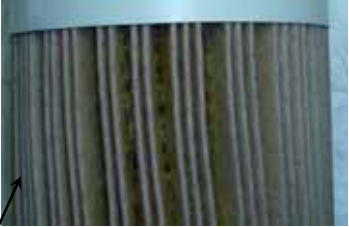
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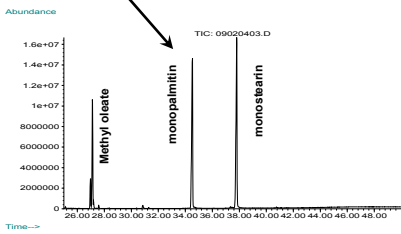
Accumulation of SMG on the Fuel Filter Caused Truck Failure

- ❑ Fuel spiked with SMG at 250 mg/L resulted in operability failure
 - SMG on filter confirmed by GC-MS
- ❑ Fuel spiked with SMG at 200 mg/L resulted in high ΔP and restricted fuel re-circulation
 - Predicted failure with 210L of additional fuel
- ❑ Fuel spiked with SMG at 150 mg/L resulted in high ΔP without fuel re-circulation problem
 - Predicted failure with 147L of additional fuel

At 250 mg/L SMG



SMG Confirmed by GC-MS for 250 mg/L and 150 mg/L



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Conclusions: SMG a Real Problem

Lab Tests

- ❑ Confirmed prior literature regarding negative impact of SMG
 - Unsaturated monoglycerides do not plug filters
 - Filters with high FBT are enriched in SMG
- ❑ FBT correlates relatively well with SMG content

AWCD Tests

- ❑ Based on spiking methodology used, SMG accumulate on the fuel filter, do not re-dissolve in the fuel and eventually will cause operability problems

Imperial Oil reports can be found on www.cpqi.ca web site

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Bio-Diesel Furnace Program

- Long term furnace operability study with bio-fuels underway
 - Evaluation of B5-B20 content fuel
- Riello burner and Kerr furnace are widely used in the marketplace
 - Riello burner BF3 Model, nozzle 0.5 USGPH, flame detector 5KΩ to 50KΩ, furnace 1200 CFM
- Furnace cycles defined with Riello, Kerr & IOL
- Total 120 days (4 months) per test cycle
 - 5 min on/20 off simulating Spring/Fall
 - 10 min on/10 min off simulating start-up endurance
 - 20 min on/10 min off simulating Winter cold snap
- Input provided by CPPI
- Test 1 & 2 completed successfully



Test#	Bio-Fuels	Start	End
1	B0, B5 & B20 CME	16-Apr-08	25-Aug-08
2	B10 TME, B20 CME & B20 SME	29-Aug-08	12-Jan-09
3	B20 TME, B15CME/B5TME, B15 SME/B5TME	19-Feb-09	30-Jun-09

Weekly Monitored Properties
 Smoke No., CO, CO₂, O₂ NO, efficiency, nozzle/pump temperature, breach temp., excess air, over fire draft, cad cell resistance